# A preliminary characterization of greenhouse gas ($CH_4$ and $CO_2$) emissions from Gulf of Cadiz mud volcanoes

## *Caracterización preliminar de emisiones de gases de efecto invernadero ($CH_4$ y $CO_2$) procedentes de volcanes de fango del Golfo de Cádiz*

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**Abstract:** Mud volcanism represents an important migration pathway for methane and other gases from deeper reservoirs to the surface; however most submarine sources remain poor quantified. During SUBVENT2 cruise, water column over several mud volcanoes were surveyed for gas seepage characterization. Water samples of ROV Niskin and Rosette-CTD Niskin bottles were recovered above the Bonjardim, El Cid, Las Negras, Mercator, Algacel, Mvseis, Madrid and Yuma mud volcanoes, and at three newly discovered, mud volcano like structures, to quantify overall gases release fluxes from seabed. $CO_2$ and $CH_4$ concentrations were measured by potentiometric titration and using a gas chromatograph, respectively, in order to understand the relationship between physicochemical and geological processes. Gases concentrations decreased from shallower to deeper mud volcanoes. Values varied widely within 50 to 200 nM for $CH_4$ and between 400 to 1500 µatm for $fCO_2$. Greenhouse gases variations were large influenced by water column depth, temperature, salinity and possibly by anaerobic oxidation of methane (AOM). Our observations suggest that the emission of methane and carbon dioxide from the mud volcanoes structures studied here may be relevant at the present as a part of the carbon global cycle.

***Keywords:*** *submarine mud volcano, seepage, methane, carbon dioxide, Gulf of Cadiz*

## 1. INTRODUCTION

Understanding and quantifying ocean–atmosphere exchanges of the long-lived greenhouse gases carbon dioxide ($CO_2$) and methane ($CH_4$) is important for the global biogeochemical cycles of carbon knowledge in the context of ongoing global climate change. $CO_2$ is the most abundant greenhouse gas whereas $CH_4$ is more "virulent", despite their lower atmospheric concentrations absorbing infrared radiation approximately 300 more effectively than $CO_2$ (Naqvi *et al*., 2010). The contribution of methane to current global warming is estimated to be about 15% (Houghton & Woodwell, 1990) to the anthropogenic greenhouse effect.

One enhanced mechanism for methane release is through submarine mud volcanoes. These structures may contribute significantly to the ocean methane pool (Sauter *et al*., 2006).

In the Gulf of Cadiz, more than 60 mud volcanoes (MV) have been confirmed (Van Rensbergen *et al*., 2005 among others) by coring samples. However, apart from the abundance of these structures, there is a lack of studies in relation with their geochemical environment and seabed methane emission.

In this work we have been focused on 11 MV as a carbon source of degassing from deep reservoirs to offer an approach of the relationship between physicochemical and geological processes and to quantify the amount of gas releases to the hydrosphere.

## 2. MATERIAL AND METHODOLOGY

The data presented in this work have been collected during SUBVENT2 expedition aboard R/V Sarmiento de Gamboa in March-April 2014. A data set of multibeam bathymetry (ATLAS Hydrosweep-DS) has been obtained over mud volcanoes together with 7

Rossete-CTD stations and 10 underwater explorations by Remotely Operated Vehicle (ROV).

### 2.1 Water sampling

We have been obtained water column samples with a Seabird 911 CTD equipped with 24 x 12 L PTFE-lined Niskin bottles where water temperature and salinity have been also measured. ROV Niskin samples were recovered at discrete water depths atop MV coupled in a CTD equipped with 4 x 2.5 L.

A total of 20 ml and 500 ml sub-samples were taken immediately upon recovery of the sampler for $CH_4$ and $CO_2$ analyses, respectively. Samples for $CH_4$ determinations were preserved with saturated mercuric chloride.

The water column on top of Rosco (CTD07), New (CTD03) and Demetrio de Armas MV (CTD04) and a control zone northwards Yuma MV (CTD06) were sampled by CTD Niskin bottles (from surface to bottom seafloor) while Las Negras (D05), El Cid (D04), MVSEIS (D06), Madrid (D08) and Yuma MV (D09) were sampled atop edifices with ROV. Mercator (CTD01-D02), Algacel (CTD02-D03-D10-D11) and Bonjardim (CTD05-D07) were sampled by both methods.

### 2.2 Analytical methods

*2.2.1 Methane analysis.*

Methane was determined by gas chromatography (Bruker GC-450) with flame ionization detection (FID). A head space technique was used to extract the dissolved gas from the water sample. A volume of about 5 mL of sample was equilibrated with a volume of 5 mL of a gas, with $CH_4$ concentrations close to atmospheric concentrations (1.8 ppmv), in a 10 mL chromatography syringe. The syringe was vigorously shaken to equilibrate water samples. When equilibrium was reached, a sample of 2 mL aliquot of the headspace was injected into the gas chromatograph for its measurement. The concentrations of the gas were calculated from the measured concentration in the head space, using the functions for the solubilities given by Wiesenburg & Guinasso (1979).

*2.2.2 Dioxide carbon analyses.*

Inorganic dissolved carbon system is described by temperature, salinity, pressure, and by four measurable parameters: partial pressure or more precisely the fugacity of $CO_2$ ($fCO_2$), dissolved inorganic carbon (DIC), pH and total alkalinity (TA). If at least two of these four parameters are measured in a sample, the other two can be calculated using equilibrium constants, temperature, pressure, and salinity (Dickson *et al*., 2007).

The fugacity of $CO_2$ values were obtained through measurements of alkalinity and pH. TA (Dickson *et al*., 2007) was measured by potentiometric titration (Metrohm potentiometric titrator and combined reference glass electrode) and pH was determined in situ by potentiometry using glass electrode/reference electrode Orion 5 STAR.

## 3. REGIONAL SETTING AND STUDY AREA

The Gulf of Cadiz is situated between 9°W to 6°45´W and 34°N to 37°15´N (Fig. 1), bounded by the Iberian peninsula and Morocco, in a structurally complex convergent tectonic setting seismically active. Mud volcanoes are an insight of this activity, in close relation with the intense seabed fluid flow recorded along both, the Iberian and the African margins.

MVs of this study are widely located at the *Moroccan field*, along the middle and upper slope of the Moroccan margin at water depths between 300 to 1600 m whereas Bonjardim is located at the deep-south Portuguese margin at 3100 m depth (Fig. 1).

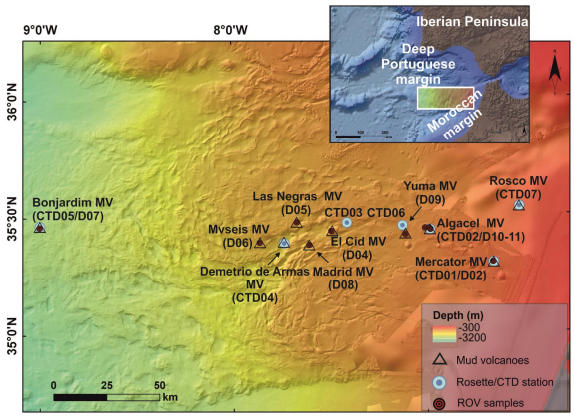


*Fig. 1. Mud volcanoes location and water samples collected during SUBVENT2 are shown.*

## 3. RESULTS

### 3.1 Methane concentrations

The concentrations of dissolved $CH_4$ in surface waters are significantly different from bottom samples. MVs measurements were variable and spanned various order of magnitude showing depth fluctuations in $CH_4$ distribution. ROV samples present similar or highest values in the sites where Rosette-CTD samples were also collected at 5-10 m above seafloor (Fig. 2).

*3.1.1 ROV samples*

Large higher concentrations were obtained of dissolved $CH_4$ from ROV samples, about 50 to 200 nM, compared with water column profile concentrations.

At Algacel MV is shown the highest value of dissolved $CH_4$ reaching 192 nM during D11 and ranging 105 to

171 nM in D10. At the near station D03 the value measured was about 83 nM. Las Negras, Mvseis, Madrid and Yuma MV present high values between 81-92 nM whereas El Cid shows variable values between 70-90 nM. Mercator MV and Bonjardim present the lowest value ranging between 50-65 nM.

### *3.1.2 Rosette CTD samples*

The higher $CH_4$ concentrations were measured during deployment of bottom samples in MV summit sites, ranging 54 to 110 nM. At Mercator MV (CTD01) this value exceeds up to 146 nM. In most cases, the concentration is higher in the bottom than in the surface excepting at Bonjardim MV (CTD05) and near Yuma MV (CTD06) which present lower bottom concentrations than the surface values (Fig.2).

Rosco, Mercator and Algacel MV present the highest values at 5 m above seafloor reaching 118, 146 and 123 nM (CTD07, CTD01 and CTD02 respectively) whereas New MV, Demetrio de Armas and Bonjardim reach their maximum concentration value of 98, 103 and 97 nM between 30 m, 1000 m and 20 m above the seafloor (CTD03, CTD04 and CTD05) respectively.

At CTD05 and CTD06, which was collected as a control zone, present a lower uniform profile in deep levels (50 nM) (significantly lower than D07 and D09 near stations which ranges between 75 and 80-90 nM respectively), which increases along water column to 75 nM in surface waters.

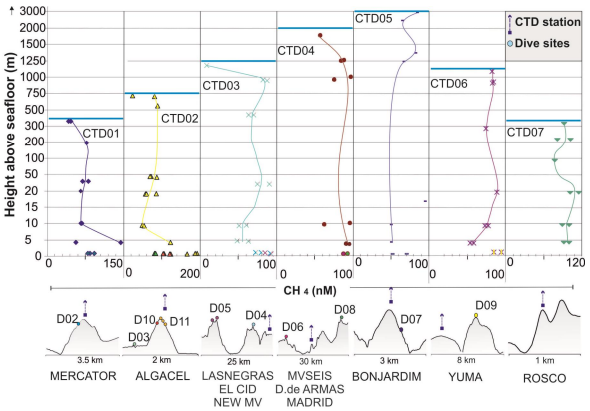


*Fig. 2. Water column profiles of methane concentrations in CTD station and ROV sampling sites.*

## 3.2 Dioxide carbon concentrations

In a general way, the concentrations of dissolved $CO_2$ are below the $fCO_2$ of 700 µatm (mean value). At Algacel MV (CTD02) and its vicinity (D03), at El Cid MV (D04) and at Mercator MV (CTD01), $fCO_2$ values exceed this limit. Dissolved $CO_2$ concentrations from ROV samples are higher than the values from Rosette-CTD samples, as has been observed for dissolved $CH_4$ concentrations.

### *3.2.1 ROV samples*

$CO_2$ concentration values of ROV samples range between 355 and 693 µatm excepting for two samples: D04 at El Cid MV with $fCO_2$ of 896 µatm and D03 (station near Algacel MV) with $fCO_2$ of 1128 µatm, showing the highest value above the seafloor.

CTD06 presents $fCO_2$ values ranging 280-440 µatm which are concentration values lower than $fCO_2$D09 (530 µatm). D03 presents higher $fCO_2$ values than the CTD02 at Algacel MV, in the same way that Yuma MV D09 and its control CTD06.

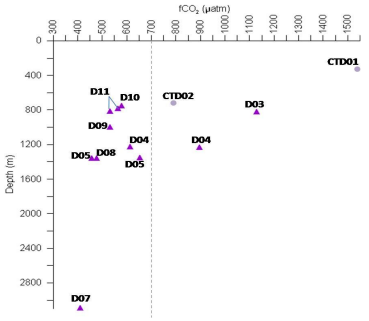


*Fig. 3. Carbon dioxid concentrations in ROV sampling sites and CTD station is shown. Samples where fugacity is higher than 700 µatm are separated by dotted line .*

### *3.2.2 Rosette CTD samples*

The concentrations of dissolved $CO_2$ in all rosette-sample profiles show a variation between 265 µatm at 10 m depth at Bonjardim MV to 1540 µatm at 341 m depth at Mercator MV (Fig. 4).

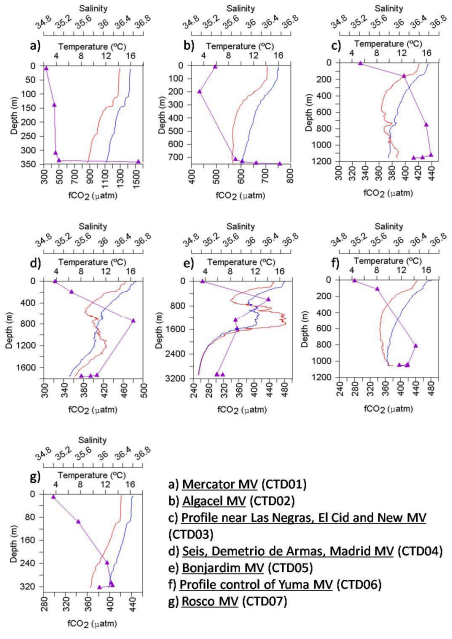


*Fig.4. Temperature, salinity and Carbon dioxid concentration (fugacity) vertical profiles in CTD-Rosette stations.*

Vertical profiles show greater $fCO_2$ values in the bottom than in the surface. Three of these profiles show an intermediate depth where there is a maximum $fCO_2$ value. CTD03 at New MV (Fig. 4C) and CTD07 at Rosco MV (Fig.4G), present this maximum near the bottom, while this maximum does not exist

in CTD04 at D. de Armas MV (Fig.4D), in CTD05 at Bonjardim MV (Fig.4E) and in CTD06 near Yuma (Fig.4F). CTD01 and CTD02 stations show also highest dissolved $CO_2$ concentrations,with $fCO_2$ (CTD01, Fig4A) of 1540 µatm at 11 m above the seafloor and fCO2 (CTD02, Fig.4B) of 756 µatm at 18 m above the seafloor.

## 4. DISCUSSION AND CONCLUSION

The high levels of methane (150 to 200 nM) in bottom waters imply that there are sites with localized, probably periodic, enhanced methane release in these mud volcanoes. This fact is more evidenced in shallower mud volcanoes seepage environments due to at Rosco, Mercator and Algacel MV, located at the shallowest water column within the study area, have been measured the highest values of dissolved $CH_4$.

Water column pressure over these structures is lower than at the deeper areas, and it allows the diffusive emission of methane easily than in others MVs. Besides, at the deepest Bonjardim MV the lowest values of dissolved $CH_4$ have been measured, possibly due to its location at 3100 m water depth and its distance from geological active Moroccan area.

Although the amount of $CH_4$ in bottom samples is very high, its concentration in the water column is moderate, mostly presenting the lower values at the water surface. This appoints that fluctuations in vertical $CH_4$ distribution may be due to anaerobic oxidation of $CH_4$ (AOM) in the water column by microbial activity (Bakker *et al*, 2014).

The regional background measured by Sommer *et al*. (2009) at Captain Arutyunov MV (CAMV), located northwards of the study area, was about 2 to 8 nM of average in vertical profiles with enhancing in situ deeper observation about 20 nM. As well as at CAMV, $CO_2$ and $CH_4$ fluxes had been measured in Sierra *et al*. (2014) at San Petersburgo MV (SPMV), located northwards CAMV.

SPMV shows dissolved $CH_4$ values decreasing from surface concentrations of 12.8 nM to high bottom concentrations, showing a maximum value of 14.29 nM above the summit of the MV. Methane fluxes measurements displayed in this study are remarkably higher in comparison with the observed in CAMV and SPMV, and other seeps locations.

In addition, bottom dissolved $CO_2$ concentrations founded in three localities of the study area, Mercator MV (CTD01), Algacel MV (CTD02 and D03) and El Cid MV (D04) are very high and correspond to values founded at depths higher than 1000 m in other regions (Pérez *et al*., 2010) although in our localities the seabed are above this depth. This anomaly could be consequent with mud volcanoes $CH_4$ and $CO_2$-rich gases discharge. Vertical profiles of dissolved $CO_2$ show lower values on surface than the bottom because of the temperature-dependent solubility of $CO_2$.Other factors such salinity or the remineralization at depth affect this vertical distribution of dissolved $CO_2$ (Lee *et al.*, 2006).

Physicochemical analyses indicate that 9 of the 11 sampling sites above mud volcanoes were seeping gases at the time of surveying; predominantly at Algacel, Mercator, Rosco and Demetrio de Armas MVs. Methane seepage from the seabed is widespread and contributes significantly to the global methane budget of the hydrosphere and also to the atmosphere.

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